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Structure and rheology of branched polyamide 6 polymers from their reaction recipe

E. van Ruymbeke, a,b J. J. M. Slot, a,c M. Kapnistas d and P. A. M. Steeman a

The structure and rheology of randomly branched polyamide melts, in particular that of branched polyamide 6, are predicted on the basis of their initial reaction recipe. To this end, a Monte Carlo approach has been developed in order to build different molecular architectures from the initial reactant monomers at the appropriate conversion level. This approach allows us to analyze the composition of these melts in terms of topological architecture and molecular weight of the various polymer species present. Subsequently, the linear rheology of each sample is predicted within the tube model framework [van Ruymbeke et al., Macromol. 2006], based on the position/seniority of the different branches in these polymer species, by averaging over a limited number of representative segments. This approach allows us to discuss the role the different polymer architectures play in the overall viscoelastic response, the importance of the different initial monomers to adequately tune the composition (and thus the rheology) of these branched systems and the necessity of reaching a high conversion level in order to obtain a large zero-shear viscosity. We also extend this approach by applying a bimodal distribution to describe the solid state polycondensation of these products. The predictions are in good agreement with experiments. This method may be applied to any branched polymer product that is synthesized via a melt condensation type reaction and can be used as a tool to test and screen in detail the flow properties of materials without prior synthesis.

1 Introduction

Relating the synthesis to the flow behavior and the final mechanical properties of polymers has been a long lasting quest in the polymer community and in particular the polymer industry. It is a crucial step in designing new materials in an economic way. In the past, by making use of very careful synthesis routes, entangled model polymers of various architectures4–7 were produced, whose rheological properties were studied. It was observed that such molecules show characteristic features in their rheological behavior that reflect their molecular structure. 8–11

The key concept here is the hierarchy of relaxation motion. In other words, entanglements belonging to topologically different parts of the macromolecule (branches or backbones or different layers) relax in a certain sequence, obeying seniority rules according to which, the outer parts of the molecule relax first and the inner ones last; only when the relaxation of the last part has been completed, the whole molecule has relaxed.

This has been a very important step as many industrial materials typically consist of branched polymers. However, industrial materials which are very complex and polydisperse tend to smear out many of these features, rendering such a detailed mapping of little use.

This was the situation until recently when Larson,20 Park and Larson,21 van Ruymbeke et al.22 and Das et al.23 proposed models that make use of this idea. In this approach they numerically blended a large number of polymers in order to simulate the rheology of polydisperse branched polymers. Despite several shortcomings, this computational approach has proven to be very successful for industrial materials such as metallocene polyethylenes23 and industrial polydisperse blends of linear and star chains.24

However, for complex branched polymers, a very large ensemble of representative molecules (of the order of several thousands) is needed in order to correctly describe their composition,24 which makes the prediction of their viscoelastic behavior very difficult. Furthermore, it becomes very difficult to point out the specific role of the different architectures present in the sample, which is necessary in order to relate the sample composition and desired properties. In order to clarify this relationship, it seems therefore important to define a simplified set of objects, still representative of the sample, which could be used as input data for predicting the rheology.

1. Materials Science Centre, DSM Research, Geleen, The Netherlands
2. Bio and Soft Matter Group, Institute of Condensed Matter and Nanosciences, École Polytechnique de Louvain, Université catholique de Louvain, Louvain-la-Neuve, Belgium. E-mail: evelyne.vanruymbeke@uclouvain.be
3. Department of Mathematics and Computer Science, Eindhoven University of Technology, Eindhoven, The Netherlands
4. Plastika Kritis S.A., Iraklion, Crete, Greece

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This is the route we have followed here: we propose to analyze and predict the viscoelastic behavior of randomly branched polyamides based on the analysis of the seniority of the different molecular segments which are present in the sample, rather than taking into account all the complex architectures of the different molecules. These last ones are thus decomposed and classified into segments of different seniorities, and their corresponding molecular weight distributions as well as their proportion are used as input data for predicting the rheology.

In order to define this ensemble of segments of different seniorities, the statistical composition of the sample needs to be determined first, based on the synthesis recipe. Some works have already been proposed in this direction for metallocene polyethylene\textsuperscript{25–27} as well as for polydisperse polyamide samples.\textsuperscript{28–32} In the latter case, it has been shown that classical Monte Carlo statistics lead to a good approximation of the sample, which is formed by a condensation reaction process. The objective here is to propose a simplified Monte Carlo approach, which takes advantage – without losing accuracy – of the fact that we know \textit{a priori} that every generation will be described by a Flory-type molecular weight distribution and that they will all have the same average molecular weight (whatever their seniority).

In particular, we study and relate the composition and rheology of two different sets of branched PA6 polymers, obtained from different synthesis recipes: while both sets contain a larger number of acid groups (the ‘A’ groups) than amino groups (the ‘B’ groups), the first set of samples contains a tri-amine (i.e. B\textsubscript{3}) as branching unit while the second set is based on a tri-acid (i.e. A\textsubscript{3}). Furthermore, the first set only contains di-amines (B\textsubscript{2}) as chain extenders\textsuperscript{28,29} while the second set of samples contains both di-amines (B\textsubscript{2}) and di-acids (A\textsubscript{2}) (see Section II).

To this end, we first measure the molecular weight distributions (MWD) of the samples by size exclusion chromatography (SEC) as well as their viscoelastic response under dynamic frequency sweeps (see Section III.). Then, in order to determine their composition, we develop a statistical approach based on a Monte Carlo algorithm. Thanks to the two step procedure, this approach allows creating an accurate, representative ensemble of molecules in a faster way than with classical Monte Carlo algorithms\textsuperscript{29} (see Section IV.1). In order to predict their viscoelastic behavior, this ensemble of molecules is then decomposed into linear chains, and strands of different seniorities, which are used as input data in the tube model of van Ruymbeke \textit{et al.}\textsuperscript{15,16} (see Section IV.2). In that way, the ensemble of molecules can be represented by a set of a few essential architectures, without losing information regarding the overall relaxation behavior of the system.

In Section V.1, the Monte Carlo approach is applied to several linear PA6 samples obtained by solid-state post-condensation.\textsuperscript{28} This allows us to point out and discuss important discrepancies between theoretical and experimental results. Next, in Sections V.2 and V.3, the compositions of the different branched PA6 samples, resulting from the two synthesis recipes, are analyzed as a function of their conversion level, by comparing their theoretical molecular weight distributions (MWD) to their experimental MWD. Their rheological curves are also presented and discussed, in relation to their composition. Conclusions are presented in Section VI.

### II Samples

All polymers were synthesized through a polycondensation type reaction of caprolactam. More details on the polymerization procedure can be found in ref. 28.

- The linear products contain homopolymerized caprolactam end-capped by benzoic acid (see Table 1).

- The branched products need the presence of a polyfunctional (A\textsubscript{f}B\textsubscript{g} with \(f + g \geq 3\)) monomer in order to create branching.

- The first set of samples (Set 1) have been synthesized using a tri-acid as branching unit. Their molar mass control and melt stability were achieved by using a mono-functional benzoic acid unit (A\textsubscript{1}) as chain stopper. The addition of diamine (B\textsubscript{2}) was necessary for the propagation of the reaction (see Table 2). The materials were solid state post-condensed for 12 hours at 190 °C under vacuum with a small nitrogen-purge, in order to enhance

### Table 1 Synthesis recipe of linear PA6

<table>
<thead>
<tr>
<th></th>
<th>(M_\text{w} ) [g mol(^{-1})]</th>
<th>Linear 1</th>
<th>Linear 2</th>
<th>Linear 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionality</td>
<td>[mol]</td>
<td>[mol]</td>
<td>[mol]</td>
<td>[mol]</td>
</tr>
<tr>
<td>Benzoic acid (BA)</td>
<td>(A_1)</td>
<td>122.13</td>
<td>0.446</td>
<td>0.223</td>
</tr>
<tr>
<td>Aminocaproic acid (ACA)</td>
<td>(A_1B_1)</td>
<td>131.17</td>
<td>0.7624</td>
<td>0.7624</td>
</tr>
<tr>
<td>Caprolactam (CAP)</td>
<td>(A_2B_1)</td>
<td>113.16</td>
<td>0.7624</td>
<td>0.7624</td>
</tr>
</tbody>
</table>

### Table 2 Synthesis recipe of branched PA6 of Set 1

<table>
<thead>
<tr>
<th></th>
<th>(M_\text{w} ) [g mol(^{-1})]</th>
<th>Branched 1-1</th>
<th>Branched 1-2</th>
<th>Branched 1-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionality</td>
<td>[mol]</td>
<td>[mol]</td>
<td>[mol]</td>
<td>[mol]</td>
</tr>
<tr>
<td>Benzoic acid (BA)</td>
<td>(A_1)</td>
<td>122.13</td>
<td>2.00</td>
<td>1.33</td>
</tr>
<tr>
<td>Tris-caproic acid melamine (TCAM)</td>
<td>(A_3)</td>
<td>468.53</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Hexamethylene diamine (HMDA)</td>
<td>(B_2)</td>
<td>116.21</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Aminocaproic acid (ACA) with (\text{NH}_2/\text{COOH})</td>
<td>(A_1B_1)</td>
<td>131.17</td>
<td>3.42</td>
<td>3.42</td>
</tr>
<tr>
<td>Caprolactam (CAP) with (\text{NH}_2/\text{COOH})</td>
<td>(A_2B_1)</td>
<td>113.16</td>
<td>356.65</td>
<td>356.65</td>
</tr>
<tr>
<td>Benzoic acid (BA)</td>
<td>(A_1)</td>
<td>122.13</td>
<td>0.9918</td>
<td>0.99360</td>
</tr>
</tbody>
</table>

\(a\) At equilibrium.
Table 3  Synthesis recipe of branched PA6 of Set 2

<table>
<thead>
<tr>
<th>Functionality</th>
<th>( M_m ) [g mol(^{-1})]</th>
<th>Recipe [mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid (BA) (A(_1))</td>
<td>122.13</td>
<td>1.94</td>
</tr>
<tr>
<td>Adipic acid (AA) (A(_2))</td>
<td>146.14</td>
<td>1.58</td>
</tr>
<tr>
<td>Bis(hexamethylene) triamine (B(_1))</td>
<td>215.22</td>
<td>1.00</td>
</tr>
<tr>
<td>Hexamethylenediadmine (HMDA) (B(_2))</td>
<td>116.21</td>
<td>0.83</td>
</tr>
<tr>
<td>Caprolactam (CAP) (A(_1)B(_1))</td>
<td>113.16</td>
<td>360.00</td>
</tr>
</tbody>
</table>

\(^a\) At equilibrium.

Branching. Table 2 contains the molar ratios after removing the estimated unreacted caprolactam. Containing a larger amount of end-cappers (A\(_i\)) compared to samples Br1-2 and Br1-3, sample Br1-1 is expected to contain a smaller amount of complex architectures at the same conversion level. On the other hand, since the ratio A\(_1\)/A\(_2\)/B\(_2\) is equal for samples Br1-2 and Br1-3, it is expected that at same conversion level, these two samples contain the same architectures. However, since sample Br1-3 contains a relatively higher amount of caprolactam, the average molecular weight of its A\(_2\), B\(_1\), and A\(_1\)B\(_1\) strands is expected to be larger than in sample Br1-2.

In contrast, the second set of samples (Set 2) have been produced based on a recipe which consists of caprolactam, mono-carboxylic (A\(_1\)) and bi-carboxylic (A\(_2\)) acids, bi-amine (B\(_2\)) and tri-amine (B\(_3\)), see Table 3. In this case, the extent of branching is controlled by the amount of the tri-amine. Four different branched materials were obtained by polymerizing this recipe to different degrees of conversion. The recipe after removing excess (unreacted) caprolactam is shown in Table 3.

### III  Experimental

#### III.1  Size exclusion chromatography

The molecular structure was determined by size exclusion chromatography (SEC). We have used a Hewlett Packard 1090M2 with RI (Refractive Index), DV (Differential Viscometer) and LS (Light Scattering, 90°) and triple detector. Since in the triple approach, light scattering is used as an absolute detector, no calibration curve is required. Furthermore, the fact that the signal is detected based on the intensity of scattered light allows obtaining a good determination of the different molecular weights, despite the presence of branched chains. Electrolyte effects were suppressed by adding 0.1 wt% of potassium-trifluoro-acetate salt. The sample solution was filtered over a 0.45 μm filter before injection and measured at 35 °C. The average molecular weights of the samples are shown in Table 4.

#### III.2  Linear viscoelasticity measurements

The measurements were conducted on a strain-controlled rheometer, from TA Instruments (ARES-2KFRTN1), equipped with an air/nitrogen convection oven and a liquid nitrogen supply, achieving temperatures between \(-140\) °C to \(+500\) °C (±0.1 °C). A parallel plate geometry (25 mm in diameter) was chosen.

It is well-known that polyamide is very sensitive to moisture which plasticizes the material. In order to keep this effect under control all samples were dried at 90–95 °C for a minimum of 1–3 days and then kept in closed glass containers. The sample pellets were loaded, melted and measured at 230 °C or 260 °C, between the two parallel plates forming 1.5–2.0 mm thick discs. Regardless of the measurement temperature, all experimental data points shown in the study have been shifted to a reference temperature of 260 °C. Drying of the polyamide samples pushes the condensation reaction out of equilibrium. This means that rheological measurements are time dependent. In order to remove this artifact, a sequence of short oscillatory frequency measurements (or a multi-frequency time sweep), from 0.1 to 100 rad s\(^{-1}\), were performed and the data points were extrapolated to zero time, obtaining the initial (undisturbed) rheological curve.

### IV  Modeling

#### IV.1  Statistical composition of branched polyamide 6

**IV.1.1  Two step-Monte Carlo algorithm.** Polyamide 6 is formed in a condensation reaction process. The recipe specifies the type and molar ratios of the initial monomeric reactants. Each monomer carries one or more reactive groups of type A (e.g. −COOH) and/or of type B (e.g. −NH\(_3\)). An A-group might

### Table 4  Structural information of the PA6 samples

<table>
<thead>
<tr>
<th>Label</th>
<th>[(\eta]) (dl g(^{-1}))</th>
<th>COOH(^a) (meq kg(^{-1}))</th>
<th>NH(_3)(^a) (meq kg(^{-1}))</th>
<th>(M_n)(^b) (kg mol(^{-1}))</th>
<th>(M_m)(^b) (kg mol(^{-1}))</th>
<th>[(\eta]) (Pa s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear 1</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>25</td>
<td>1.14</td>
</tr>
<tr>
<td>Linear 2</td>
<td></td>
<td></td>
<td></td>
<td>12.9</td>
<td>36</td>
<td>1.50</td>
</tr>
<tr>
<td>Linear 3</td>
<td></td>
<td></td>
<td></td>
<td>21.6</td>
<td>54</td>
<td>1.82</td>
</tr>
<tr>
<td>Set 1: Branched 1-1</td>
<td>/</td>
<td>/</td>
<td></td>
<td>11.8</td>
<td>40</td>
<td>1.31</td>
</tr>
<tr>
<td>Set 1: Branched 1-2</td>
<td>/</td>
<td>/</td>
<td></td>
<td>14.4</td>
<td>56</td>
<td>1.61</td>
</tr>
<tr>
<td>Set 1: Branched 1-3</td>
<td>/</td>
<td>/</td>
<td></td>
<td>16</td>
<td>56</td>
<td>1.64</td>
</tr>
<tr>
<td>Set 2: Branched 2-1</td>
<td>1.10</td>
<td>60</td>
<td>64</td>
<td>15(^b)</td>
<td>32(^b)</td>
<td>1.1</td>
</tr>
<tr>
<td>Set 2: Branched 2-2</td>
<td>1.41</td>
<td>39</td>
<td>40</td>
<td>19(^b)</td>
<td>51(^b)</td>
<td>1.41</td>
</tr>
<tr>
<td>Set 2: Branched 2-3</td>
<td>1.52</td>
<td>36</td>
<td>35</td>
<td>19(^b)</td>
<td>57(^b)</td>
<td>1.52</td>
</tr>
<tr>
<td>Set 2: Branched 2-4</td>
<td>1.71</td>
<td>29</td>
<td>30</td>
<td>24(^b)</td>
<td>77(^b)</td>
<td>1.71</td>
</tr>
</tbody>
</table>

\(^a\) Determined by end-group titration. \(^b\) Determined by triple SEC.
react with a B-group, chemically binding the monomer units to which the two groups are attached and forming one molecule of water as a byproduct. The water is partially removed from the system and thus control is achieved over the degree of polymerization. Mono-functional monomers (A1), having only one reactive group, act as chain stoppers, bi-functional ones (with two reactive groups) as chain extenders, and multifunctional ones (more than three functional groups) as branching points.

Regarding the reaction modeling, the following assumptions are made:13,14 (1) an A-group reacts only with a B-group and vice versa; (2) all reactions have equal probability; (3) no intramolecular reactions occur, i.e. no cycles are formed. These assumptions allow us to reduce the number of possible architectures present in the sample and, as described in this section, to develop a convenient approach for determining the most probable composition. Furthermore, by keeping a well-defined ensemble of different molecules, it allows us to relate sample composition to rheological behavior. However, these assumptions could lead to some deviations between the real and predicted composition. In particular, some studies on linear PA molecules are of (located between two extremities or functional groups A, of the same average molecular weight M0,Strand, and (2) we know, a priori, that every chain extremity is of type \( \text{A} \) (real or virtual).19–23 In contrast to the actual polycondensation process and to usual Monte Carlo algorithms, the molecules are therefore not built from the different monomers (A1B1, B2, A3, ...), but directly from specific sub-chains which can be considered as building blocks of the molecules. These subchains are defined as the smallest molecules having all their extremities of type \( \text{A} \). They can contain one or more A1B1 –...– A3B3 strands.

Thus, in step 1, all possible short subchains which are “closed” only by acid groups \( \text{A} \) are built (from the A1B1 strands) while in step 2, we consider the possibility for these subchains to be linked together, \( \text{via} \) the B2 or B3 monomers, in order to create larger (branched) molecules. Using this procedure, we therefore build the “skeleton” of each of the molecules, which represents all the necessary information to describe the real molecule.

**Step 1.** The different possible subchains which are “closed” by only acid groups are represented in Fig. 1 for the first or the second set of branched PA6: in Set 1, they all contain either one end-capper \( \text{A}_1 \) or \( \text{A}_i \), or one \( \text{A}_3 \) to which three \( \text{A}_1 \)B1 strands are coupled. The numbers of these different subchains are thus directly determined from the number of \( \text{A}_1 \), \( \text{A}_i \) and \( \text{A}_3 \) in the reaction recipe. In the second step of the algorithm, the B2 monomers will be added and these subchains will be able to assemble. For the second set of branched PA6, Set 2, the subchains, which can be closed by ‘\( \text{A} \)’ groups contain either one strand closed by one \( \text{A}_1 \) or one \( \text{A}_i \), or two A1B1 strands associated \( \text{via} \) a \( \text{A}_3 \) (see Fig. 1). These strands will be linked \( \text{via} \) a \( \text{B}_2 \) or a \( \text{B}_3 \) in the second step of the algorithm.

**Step 2.** As already mentioned, in the second step of the algorithm, the molecules are built one by one, in a random way, based on the probability that an \( \text{A}_1 \)B1 end-group of a subchain defined in step 1 reacts with a \( \text{B}_2 \) or a \( \text{B}_3 \) monomer and then becomes linked to other subchains. It must be noted that end-cappers \( \text{A}_1 \) and \( \text{A}_i \) can never react with a group \( \text{B} \) and that an \( \text{A}_1 \)B1 end-group will not necessarily react with a \( \text{B}_2 \) group. Its reaction probability is determined by the ratio between the number \( \text{B} \) sites and the number of \( \text{A}_1 \)B1 end-groups still available “in the box”:

\[
p(\text{to link a strand to a } \text{B}_2 \text{ monomer}) = \frac{2B_{up}^{\text{B}_2}}{3A_1^{up} + A_i^{up} + A_3^{up}} \quad (1)
\]

for Set 1, and

\[
p(\text{to link a strand to a } \text{B}_2 \text{ monomer}) = \frac{2B_{up}^{\text{B}_2}}{2A_1^{up} + A_i^{up} + A_3^{up}} \quad (2)
\]

\[
p(\text{to link a strand to a } \text{B}_2 \text{ monomer}) = \frac{3B_{up}^{\text{B}_2}}{2A_1^{up} + A_i^{up} + A_3^{up}} \quad (3)
\]

where \( B_{up}^{\text{B}_2} \) (\( B_{up}^{\text{B}_3} \)) represents the updated number of \( \text{B}_2 \) (\( \text{B}_3 \)) monomers, which are still available “in the box”, \( A_1^{up} \) represents

![Fig. 1 Cartoon of the preliminary subchains used as building blocks for the two sets of samples. Their end-groups must be ‘\( \text{A} \)’ groups.](image)
the updated number of star-like subchains composed of three strands and $A_{1}^{\text{up}} + A_{1}^{\text{up}}$ represents the updated number of linear subchains composed of one strand (and thus, containing only one $A_{1}B_{1}$ end-group).

Once a $B_{2}$ ($B_{3}$) monomer is added to a building block, one (two) new subchain(s) will be also added since all end-chains must end by an ‘A’ group. For Set 1, the probability for a $B_{2}$ monomer to react with a specific subchain (see Fig. 1) depends on the number proportion of strands belonging to these subchains:

\[
p(\text{to link the $B_{2}$ monomer to a subchain containing an $A_{1}$}) = \frac{3A_{1}^{\text{up}}}{3A_{1}^{\text{up}} + A_{1}^{\text{up}} + A_{1}^{\text{up}}}
\]

\[
p(\text{to link the $B_{2}$ monomer to a subchain containing an $A_{1}'$}) = \frac{A_{1}'^{\text{up}}}{3A_{1}^{\text{up}} + A_{1}^{\text{up}} + A_{1}^{\text{up}}}
\]

\[
p(\text{to link the $B_{2}$ monomer to a subchain containing an $A_{1}$}) = \frac{A_{1}^{\text{up}}}{3A_{1}^{\text{up}} + A_{1}^{\text{up}} + A_{1}^{\text{up}}}
\]

Similiar equations can be derived for the two reaction sites available on the $B_{3}$ monomers. As long as there are new $A_{1}B_{1}$ end-groups added to the molecules, which are susceptible to react with a $B_{2}$ ($B_{3}$) monomer, this procedure needs to be repeated. Once the molecule does not contain any A group left that can still react, the molecule is complete. Its related information is stored (see Section IV.1.3), and we can start building another molecule.

It must be noted that adding $A_{1}B_{1}$ monomers to a sample will not change the architecture (or skeleton) of the molecules. However, it will increase the average molecular weight of every strand, $M_{n,\text{Strand}}$ (see Section IV.1.2).

Usually, in this study, the ensemble of chains counted $2 \times 10^{4}$ to $2 \times 10^{5}$ virtual molecules. The average molecular properties of our Monte Carlo simulated ensembles have been validated against the analytical results for $M_{n}$, $M_{w}$ and $M_{z}$ as given by Durand and Bruneau and by Fradet and Tessier.

**IV.1.2 Average molecular weights.** The main average molecular weights of the samples can be determined from their synthesis recipe. This requires, first, determining the number of virtual $A_{1}$ units present in the sample, which accounts for the non-reacted $B$ groups. This number depends on the conversion level $p_{A_{1}}$ is determined using the following relationships:

\[
p_{A} = \frac{\text{reacted “B”}}{\text{total “A”}} = \frac{2B_{2} + AB}{3A_{1} + A_{1} + A_{1} + AB}
\]

for Set 1, (7)

\[
p_{A} = \frac{\text{reacted “B”}}{\text{total “A”}} = \frac{2B_{2} + 3B_{1} + AB}{2A_{2} + A_{1} + A_{1} + AB}
\]

for Set 2. (8)

Then, the average molecular weight in number of a strand, $M_{n,\text{Strand}}$, is determined, based on the fact that the number of strands, $n_{\text{chains}}$, does not depend on the $B_{x}$ monomers (these monomers allow linking two strands together but do not generate new strands) and that on every $A_{x}$ will be fixed $x$ strands:

\[
M_{n,\text{Strand}} = \frac{A_{1}M_{w,A_{1}} + A_{1}M_{w,A_{1}} + B_{2}M_{w,B_{2}} + AB M_{w,AB}}{n_{\text{chains}}}
\]

for Set 1, (9)

\[
M_{n,\text{Strand}} = \frac{A_{1}M_{w,A_{1}} + A_{1}M_{w,A_{1}} + B_{2}M_{w,B_{2}} + B_{1}M_{w,B_{1}} + AB M_{w,AB}}{n_{\text{chains}}}
\]

for Set 2, (10)

with $M_{w,A_{1}}$ and $M_{w,B_{x}}$ being the weight of the corresponding monomers.

In order to determine the average molecular weight in number of the whole sample, $M_{n,\text{total}}$, the average number of chains in the sample, $n_{\text{chains}}$, is calculated, based on the fact that any $A_{x}$ will generate a new molecule apart from the case where it is combined with a $B_{x}$ monomer (then, it will simply be added to an existing molecule). Therefore:

\[
n_{\text{chains}} = A_{3} + A_{1} + A_{1} - B_{2}
\]

for Set 1, (11)

\[
n_{\text{chains}} = A_{2} + A_{1} + A_{1} - B_{2} - 2B_{3}
\]

for Set 2, (12)

These results have been validated by comparing the average molecular weights from eqn (14) to the average molecular weight determined by using either the analytic method proposed in ref. 32 or a classical Monte Carlo approach developed in ref. 29. As an example, the total average molecular weight $M_{n,\text{total}}$ for sample Br1-1 (see Table 2) at a conversion $p_{A_{1}} = ‘A’/‘B’ = 0.99099$ is equal to 18.1 kg mol$^{-1}$, based on the analytic method, and 18.2 kg mol$^{-1}$ based on the classical Monte Carlo approach while from eqn (14) $M_{n,\text{total}}$ is equal to 18.157 kg mol$^{-1}$.

Furthermore, as explained in Section V.2, the total average molecular weight, $M_{n,\text{total}}$, can also be determined directly from the two-step Monte Carlo approach proposed here. Again, the agreement between these methods is very good (see Table 6 and 8), validating eqn (14) and (16).
IV.1.3 Output data. Useful information must be drawn from the two step Monte Carlo algorithm, in order to determine the sample molecular weight distribution and to be able to predict their linear viscoelastic behavior. To do so, two matrices are continually updated during the creation of the new molecules:

- A first matrix with elements $N_{\text{number}}(i,j)$, counting the number of molecules containing $i$ strands and $j – 1$ branching points.
- A second matrix with elements $A_{\text{number}}(k,l)$, counting the number of molecules with $k$ strands and $l$ monomers ($A_1$ or $A_1$) monomers. This matrix will be needed for samples of Set 1, in order to determine if the dangling branches contain one or two strands (see Section IV.1.5).

At the end of the algorithm, these matrices are normalized in order to represent the number proportion of a specific class of molecules. Their corresponding matrices in weight proportion, $N_{\text{weight}}(i,j)$ and $A_{\text{weight}}(i,j)$, are then determined by multiplying these number proportions by the number of strands in the corresponding molecules and by normalizing the matrices.

In addition to these matrices, the total number of segments with seniority 2, i.e. those segments that are linked at one end to two dangling ends, is directly determined in the algorithm, by analyzing the sequence of elements taken “from the box”. As is shown in Section V.2, for the samples analyzed in this work, the proportion of deeper segments, with seniority 3 or more, is so low (below the entanglement limit) that they do not need to be quantified further.

IV.1.4 Molecular weight distribution of the whole sample. In order to compare experimental and theoretical data, the theoretical molecular weight distribution of the whole sample must be determined. As already mentioned in Section IV.1.1, any strand of any molecule in the sample has the same average molecular weight, and can be described by a Flory distribution, with a polydispersity of 2. Therefore, in addition to this average molecular weight $M_{n,\text{Strand}}$, we only need to know the weight proportions, $\varphi_S$, of chains containing a number $S$ of strands (whatever the number of branching points, $Br$) in order to calculate the final distribution:

$$\varphi_S = \sum_{Br} N_{\text{weight}}(S, Br)$$

(17)

The molecular weight distributions, MWDs, corresponding to the chains containing $S$ strands are then determined as in ref. 24 and 30, based on the fact that association between two strands of mass $M_i$ and $M_j$ is proportional to the product of the number proportions of these strands. Representative results are shown in Fig. 2: as expected, the distribution MWDs resulting from the association of $S$ strands, i.e. of $S$ Flory distributions of mass $M_{n,\text{Strand}}$, leads to a distribution described by $M_n = SM_{n,\text{Strand}}$ and $M_w = (1 + 1/S)M_{n,\text{Strand}}$.

The final MWD of the whole sample is then determined, by summing up all the MWDs of the various distributions weighted by their proportion $\varphi_S$:

$$\text{MWD} = \sum_S \varphi_S \text{MWDs}$$

(18)

which can be compared to experimental SEC data.

IV.1.5 Classification of the molecular segments by seniority. Several molecular architectures are present in the samples. In order to predict the corresponding linear viscoelastic behavior, the different molecular segments need to be classified according to their seniority, based on the output data (see Section IV.1.3). Since, in the case studied here, only few molecular segments have a seniority equal to 3 or more, we limited this classification to linear chains, star molecules (i.e. with one branching point), dangling branches (i.e. branches with a seniority of 1), segments with a seniority of 2 and segments with a seniority of at least 3. It must be noted that the star molecules are also included in the dangling branches category and, therefore, do not need to be treated separately. However, in order to discuss the sample composition, it is interesting to determine their proportion.

Set 1. The proportion of linear chains in a sample of Set 1 is directly obtained from the output data (no branching point). The proportion of the dangling branches of a molecule composed of $S$ strands and $Br$ branching points can be determined as:

$$\text{prop}_{\text{Dangling Branches}}(S, Br) = \frac{S - 2(2Br - 1)}{S}, \text{ for } Br \geq 1.$$

(19)

This result is based on the fact that every segment of seniority equal to or greater than 2 is composed of two $A_1B_1$ strands linked by a $B_2$ monomer (see Fig. 3).

As illustrated in Fig. 3, these dangling branches are composed of either one or two $A_1B_1 \ldots A_1B_1$ strands, i.e. are either ‘simple’ or ‘double’. The ‘double’ dangling branches are necessarily closed by a $A_1$ end-capper. Their corresponding weight proportions can therefore be determined on this basis.
prop (‘double’ dangling branches) = \frac{2A_1}{\# \text{Strands}} \quad \text{for } Br \geq 1. \quad (20)

On the other hand, the proportion of segments of seniority 2 is determined step by step, in the algorithm, based on the sequence according to which the subchains and the linkers are randomly taken. From the recipe, we know - \textit{a priori} - that any inner segment is double, i.e. is composed of two strands linked by a B2 chain extender.

Set 2. In order to determine the seniority of molecular segments of a sample of Set 2, a similar approach as with Set 1 is used. Since in this case, both chain extenders B2 and A2 are present in the recipe, every molecular segment can contain up to a large number of strands, as illustrated in Fig. 4.

Therefore, as explained in Section V.3, rather than considering molecular segments with 1, 2, or more A1B1 - … - A1B1 strands, we define and work with larger strands, which contain all the monomers located between one extremity/branching point and another extremity/branching point of the molecule. Thus, these large strands also include chain extenders B2. All these large strands are described by the same MWD (see Section V.3). Therefore, the proportion of the ‘large’ dangling branches in a molecule only depends on its number of branching points Br (B2):

\[ \text{prop Dangling Branches} (S, Br) = \frac{2 + Br}{1 + 2Br} \quad (21) \]

As for samples of Set 1, the proportion of large strands of seniority 2 is determined based on the sequence according to which the sub-chains and the linkers are randomly taken. In contrast to samples of Set 1, the inner segments of Set 2 samples have the same average length as the dangling branches.

IV.2 Tube modeling

IV.2.1 Relaxation function. In order to predict the LVE of the blends, we use the time-marching algorithm (TMA) developed in previous works for predicting the linear viscoelasticity of linear, star,22 H, pompon13-36 and tree-like36,37 polymers. This tube-based model expresses the stress relaxation function \( G(t) \) of the polymer at time \( t \) by taking into account both the high frequency Rouse relaxation of the polymer38 and the disentanglement relaxation function \( G_d(t) \), which includes a classical description of reptation, contour length fluctuations, and constraint release processes.1,38-41

\[
G(t) = G_d(t) + \sum_i \frac{\rho R T}{M_i} \sum_{p=1}^{4} \exp \left( \frac{-p^2 t}{\tau_k(M_i)} \right) + \frac{1}{4} \rho R T \sum_{p=1}^{2} \exp \left( \frac{-p^2 t}{\tau_k(M_i)} \right) \]

\[
G_d(t) = G_d^n \left( \sum_i \left( \phi_{\text{linear},i} \right) p_{\text{rept}}(x_{\text{lin},i}, t) \right) \phi_{\text{fluc}}(x_{\text{lin},i}, t) dx_{\text{lin},i} \]

(22)

where \( G_d^n \) is the plateau modulus, \( \phi_{\text{linear},i} \) and \( \phi_{\text{fluc}} \) are the weight fractions of the different linear chains and of the segments of seniority \( J \) of the polymer \( G \) in the polymer, \( \rho \) is the polymer density, \( T \) is the temperature and \( \tau_k(M_i) \) is the Rouse relaxation time of a chain of mass \( M_i \) and proportion \( \phi_i \). Furthermore \( p_{\text{rept}}(x,t) \) and \( p_{\text{fluc}}(x,t) \) are the survival probabilities of the initial tube segments localized at the normalized position \( x \) (going from 0 at the chain extremity to 1 at the middle) at time \( t \), for the reptation and contour length fluctuations processes, respectively. The \((a+1)\) exponent takes into account the dynamic tube dilution process, with the dynamic dilution exponent \( a \) being fixed to 1.42 Since the molecular segments are rather short and their corresponding relaxation times are not well separated, we assume that tension equilibration process does not influence the relaxation of the deeper generations.43 It must be noted that possible reptation of a complex, branched molecule is not considered. Indeed, as was shown in a previous work,44 its influence is expected to be negligible. By summing up the survival probabilities along all the chains according to their proportion at time \( t \), the total unrelaxed fraction of the polymer at this specific time, \( \Phi(t) \), is then obtained.

As explained in ref. 13, the survival probabilities \( p_{\text{rept}}(x,t) \) and \( p_{\text{fluc}}(x,t) \) can be described by time-decreasing exponential functions depending, respectively, on the reptation and fluctuation times of the different molecular segments along the molecules. Thereby taking into account the polymer fraction that is already relaxed in the form of solvent speeds-up the relaxation of the remaining initial tube segments. Due to the large number of different architectures, this fraction, that must be known in order to determine the relaxation time of the different tube segments at time \( t \), cannot be determined \emph{a priori}, as a function of its localization. Therefore, as proposed in ref. 13, we rather define it in every time step, and use the value determined in the previous time step, \( \Phi(t - \Delta t) \), to approximate the remaining initial tube fraction at time \( t \).

For complex molecules, one can describe the hierarchical relaxation by CLFs of the segments of different seniorities, starting from the outer layers (dangling branches) toward the central branching point. The corresponding fluctuation times of any part of the molecule are then determined, by taking the extra friction coming from the branches on the motion of
deeper segments (of seniority 2 or more) into account. In order to ensure the continuity among the fluctuation times of the different generations, different reference coordinate systems are used.\textsuperscript{13,16}

Finally, from the relaxation function $G(t)$, the storage and loss moduli are determined using the Schwarzl functions.\textsuperscript{43}

IV.2.2 Representative segments for predicting the viscoelastic properties. In order to predict the linear viscoelastic behavior of these polydisperse samples, a representative ensemble of segments, which will be considered as input data in the tube model, and which should involve a minimum number of components, must be defined. To do so, as already mentioned, all segments of a specific seniority (linear chains, dangling branches, segments of seniority 2 and deeper segments) are analyzed in one go, rather than analyzing every molecule one by one. (Note that with the samples proposed in this work, the proportion of segments of seniority 3 or deeper segments is so low that they will be considered as “untangled chains” as soon as the segments of seniority 2 are relaxed (see Part IV.2.3)) The MWDs of these specific generations are divided into eight representative molecular weights, following the procedure described in ref. 24. While the relaxation times of the linear chains and of the dangling branches only require analyzing these eight strands of different masses, the determination of the relaxation times on a segment of seniority 2 requires considering all possible combinations between two dangling ends (of seniority 1) and the segment of seniority 2, \textit{i.e.} with $8^2 = 512$ combinations. However this last number is reduced to 288 combinations by combining the pairs of dangling branches $(M_i, M_j)$ and $(M_j, M_i)$ (with $i \neq j$). Furthermore, the longest relaxation times of the dangling branches attached to the segments of seniority 2, which are needed to determine the fluctuation times of the deep segments, are already known.

It must be noted that by determining the relaxation times of all segments of the same species, it is assumed that only the linear chains can relax by reptation. Thus, some specific architectures such as a star chain with one short arm and two long arms, or a comb chain with short branches, which could, a priori, reptate, are considered here as relaxing only by CLF or constraint release. The validity of this assumption has been checked and as in ref. 24 for samples with similar polydispersity this approximation does not significantly influence the results.

IV.2.3 Disentanglement limit. The fact that the relaxed part of the polymer will act as a solvent for the remaining the oriented polymer fraction is taken into account by the dynamic dilution process (DTD), which considers that the chains are moving in a dilated tube. The diameter of this last tube is determined on the basis of the effective molecular weight between two entanglements, $M_e(t)$, which is defined to be equal to $M_e(t = 0)/\Phi(t)$.\textsuperscript{41} The effective molecular weight between two entanglements will thus increase with time. At some point, when the molecular weight of the chain becomes shorter than $2M_e(t)$, the chains are not (effectively) entangled anymore and will relax according a Rouse process rather than by reptation or CLFs. This needs to be taken into account in the model, especially with dendritic structures, where the fluctuation times of the deeper generations are predicted to be very long (see Section V.2).

IV.2.4 Material parameters. The tube model requires the specification of three material parameters: the plateau modulus, $G^*_0$, the molecular weight between two entanglements, $M_e,0$ and the Rouse time of an entanglement segment, $\tau_e$. Using a best-fit procedure on the set of linear PA6 samples, their values have been determined here to be 1.8 MPa, 2 kg mol\textsuperscript{-1} and 1.9 $10^{-7}$ s respectively, at 260 °C. The dynamic dilution exponent $\alpha$ has been fixed to 1.

V Results

V.1 Linear PA6 samples

V.1.1 Composition. Based on Table 1, the average molecular weight $M_n$ of the linear PA6 polymers at full conversion can be determined and is equal to 25.4 kg mol\textsuperscript{-1} ($P_{A,\text{max}} = 0.995$) for Lin 1, 50.8 kg mol\textsuperscript{-1} ($P_{A,\text{max}} = 0.9975$) for Lin 2 and infinite ($P_{A,\text{max}} = 1$) for Lin 3.\textsuperscript{29} However, the real average molecular weights of the chains are much lower, as shown in Table 4, which corresponds to conversion levels of the ‘A’ groups (or acid groups), $P_A$, lower than these maximum values. Whatever the conversion level, the statistical MWD will always lead to a Flory distribution.\textsuperscript{32}

Despite the fact that, in theory, the polydispersity of linear PA6 samples should be equal to 2, a large polydispersity was measured for the linear samples Lin 1, Lin 2 and Lin 3 (see Table 1).\textsuperscript{28} This is illustrated in Fig. 5 for a representative sample, Lin 2, which compares experimental and theoretical distributions: the experimental MWD are indeed much broader than a Flory distribution. In fact, the MWD measured by SEC is well described when two Flory distributions are combined. This result, already observed in literature,\textsuperscript{45} is often attributed to the solid-state post-condensation process of the samples: during the solid-state post-condensation, a part of the end groups of the PA6 are located close to the crystalline phase and therefore, cannot easily post-condensate further. On the other hand, the chains with end-groups located in the amorphous regions can easily continue to grow. This would lead to two different speeds of solid-state post-condensation, which could explain why two different conversion levels are needed in order to fit the
experimental data. With such systems, one should therefore consider different reaction kinetics, as a function of the chain status.\footnote{\ref{33,34}}

**V.1.2 Viscoelastic properties.** The viscoelastic properties of the linear PA6 samples have been predicted by using the TMA tube model and based on their experimental MWD. As shown in Fig. 6, the agreement between the experimental and the predicted curves is very good for the three samples. This confirms that the samples are linear. Indeed, the presence of long chain branching would have led to an underestimation of the terminal relaxation times of these samples, which is not observed here.

As observed in Fig. 5, the MWD measured by size exclusion chromatography does not fit into a Flory distribution. As illustrated in Fig. 7, the same conclusions are drawn from the analysis of their rheological data: the predicted viscoelastic data based on a Flory distribution cannot correctly capture the shape of the experimental curves. By increasing the average molecular weight of the Flory distribution from 14 kg mol\(^{-1}\) to 19 kg mol\(^{-1}\), the zero shear viscosity is predicted better, due to the similarity between the average molecular weight \(M_w\) of the experimental MWD (of 36 kg mol\(^{-1}\)) and that of the Flory distribution for \(M_n = 19\) kg mol\(^{-1}\), i.e. \(M_w = 38\) kg mol\(^{-1}\). However the predicted curves still show a too low polydispersity (the relaxation peak is too narrow).

**V.2 Branched PA6 samples-Set 1**

**V.2.1 Composition.** In order to determine and analyze the different (branched) molecular architectures present in samples of Set 1, the conversion level of the acid groups ‘\(A\)’, \(p_A\), must be determined. Since this value is unknown, it is considered here as an adjustable parameter, and determined by a best-fitting procedure.

---

![Fig. 6](image-url) Comparison between the experimental (symbols) and the predicted (continuous curves) complex viscosity (a) and storage and loss moduli (b) for samples Lin 1 (■), Lin 2 (□) and Lin 3 (▲). The predictions are based on the experimental MWD.

![Fig. 7](image-url) Comparison between the experimental (symbols) and the predicted complex viscosity (a) and storage and loss moduli (b) for samples Lin 2. The predictions are based on a Flory distribution with \(M_n = 14\) kg mol\(^{-1}\) (---) or 19 kg mol\(^{-1}\) (thin ---), or on the experimental MWD (see).

---

Then, as explained in Section IV.1, the different architectures present in the samples are determined by the Monte Carlo algorithm and are classified according to their number of \(A\) and \(B\) strands and their number of branching points. The weight proportions of these different classes of molecules as a function of their number of \(A\) and \(B\) strands are shown in Fig. 8a, for sample Br1-1 and for \(p_A\) fixed to 0.9918, i.e. its maximum (equilibrium) level. Due to the synthesis recipe of these samples, every linear chain or every dangling branch contains either one strand or two strands linked together via a B monomer, which represents the only possible chain extender (see Fig. 3). The presence of the B monomers can be observed in Fig. 8a: for example, a star...

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chain (i.e. with one branching point) will contain from 3 to 6 strands (and thus, from 0 to 3 B₂ monomers).

Knowing the weight proportion of chains as a function of their number of strands, \( \varphi_{B_0} \), the MWD of the whole sample is determined [see eqn (18)]. Results obtained for sample Br1-1 and \( p_A = 0.9918 \) are shown in Fig. 8b, and compared to experimental results. In this case, it is clear that the value of the maximum conversion level is too high in order to correctly fit the experimental MWD and that a lower value must be used (see below).

Influence of the conversion level \( p_A \) on the composition. It is therefore important to study the influence of the conversion level on the sample composition for a representative sample of Set 1. As shown in Tables 5 and 6, several values of \( p_A \) have been theoretically tested for the three samples of Set 1. As discussed in the next section, these values have been chosen to discuss the composition of the experimental MWD. Based on these different conversion levels, the corresponding statistical composition of the sample has been analyzed and the architectures found were divided into different classes of segments (see Table 5). Their main average molecular weights have also been determined (see Table 6).

### Table 5  Weight proportion of segments of different seniorities, at different conversion levels, for the samples of Set 1. The proportions of linear chains and dangling branches are divided into the proportion of segments with one strand/the proportion of segments with two strands.

<table>
<thead>
<tr>
<th></th>
<th>Linear chains</th>
<th>Star arm</th>
<th>All dangling branches (including the star arm)</th>
<th>Segment of seniority 2 with ( Br = 2/Br &gt; 2 )</th>
<th>Deeper segments (( S \geq 3 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Br1-1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( p = 0.9918 ) (( A' = 0 ))</td>
<td>23.8/6.42</td>
<td>20.8/11.1</td>
<td>36.3/13.12</td>
<td>4.8/6.16</td>
<td>3.47%</td>
</tr>
<tr>
<td>( p = 0.989 )</td>
<td>33.35/8.40</td>
<td>23.5/11.6</td>
<td>33.6/16.6</td>
<td>4.0/3.0</td>
<td>1%</td>
</tr>
<tr>
<td>( p = 0.9864 )</td>
<td>40.6/9.3</td>
<td>23.6/10.8</td>
<td>3.1/1.6</td>
<td>0.7%</td>
<td></td>
</tr>
<tr>
<td><strong>Br1-2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| \( p = 0.9937 \) (\( A' = 0 \)) | 16.4/4.4 | 17.3/9.1 | 37.4/19.7 | 4.8/9.8 | 7.5%
| \( p = 0.987 \) | 39.0/9.2 | 23.7/11.1 | 31.4/14.7 | 3.3/1.8 | 0.6 |
| **Br1-3** |               |          |                                                |                                               |                               |
| \( p = 0.9952 \) (\( A'_1 = 0 \)) | 16.4/4.4 | 17.3/9.1 | 37.4/19.7 | 4.8/9.2 | 7.5%  |
| \( p = 0.9945 \) | 20.2/5.5 | 19.3/10.3 | 36.8/19.7 | 4.9/7.8 | 5.1 |
| \( p = 0.989 \) | 43.0/9.6 | 23.5/10.4 | 29.8/13.1 | 2.8/1.3 | 0.4 |

### Table 6  Predicted average molecular weight and polydispersity for samples of Set 1, as a function of their conversion level.

<table>
<thead>
<tr>
<th></th>
<th>( M_{n,Strand} ) from eqn (14)</th>
<th>( M_{n,total} ) determined by the algorithm</th>
<th>Predicted polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Br1-1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( p = 0.9918 ) (( A' = 0 ))</td>
<td>8.33</td>
<td>20.8</td>
<td>2.73</td>
</tr>
<tr>
<td>( p = 0.9905 )</td>
<td>7.6</td>
<td>16.84</td>
<td>16.83</td>
</tr>
<tr>
<td>( p = 0.989 )</td>
<td>6.91</td>
<td>13.75</td>
<td>13.74</td>
</tr>
<tr>
<td>45% ( p = 0.9918, 55% ( p = 0.9864 )</td>
<td>/</td>
<td>13.45</td>
<td>2.92</td>
</tr>
<tr>
<td><strong>Br1-2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( p = 0.9937 ) (( A' = 0 ))</td>
<td>9.6</td>
<td>31.24</td>
<td>3.17</td>
</tr>
<tr>
<td>( p = 0.987 )</td>
<td>6.14</td>
<td>11.03</td>
<td>11.01</td>
</tr>
<tr>
<td><strong>Br1-3</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( p = 0.9952 ) (( A'_1 = 0 ))</td>
<td>12.7</td>
<td>41.3</td>
<td>41.2</td>
</tr>
<tr>
<td>( p = 0.9945 )</td>
<td>11.8</td>
<td>33.1</td>
<td>33.1</td>
</tr>
<tr>
<td>( p = 0.989 )</td>
<td>6.62</td>
<td>12.6</td>
<td>12.6</td>
</tr>
</tbody>
</table>
better fit the main peak of the experimental MWD, the amount of high molecular weight chains becomes then underestimated. This is probably due to a similar reason as observed with the linear solid-state post-condensated sample (see Fig. 3), where only the chain-ends in the amorphous phase of the sample seem to post-condensate in the solid state. Thus, as proposed in Section V.1, one can try to fit the experimental distribution by combining two distributions, corresponding to two different conversion levels. As shown in Fig. 10, based on these two conversion levels, it is indeed possible to obtain a good agreement between the experimental and predicted MWD. The main architectures as well as the corresponding average molecular weights of these samples are given in Tables 5 and 6.

It must be noted that there are, a priori, several combinations that are able to adequately describe the experimental MWD. For samples Br1-1 and Br1-2 however, this number is reduced since the sample contains a non-negligible fraction of high molecular weight molecules, which can be correctly captured only by considering that the amorphous part of the sample has reached its maximum conversion level (i.e. $p_A = 0.9918$ for sample Br1-1 and $p_A = 0.9937$ for sample Br1-2).

The deviation observed at low molecular weights is most probably due to cyclic molecules, which are not taken into account in the statistical model used here.

V.2.2 Viscoelastic properties. Based on the statistical composition of these samples, their rheological behavior can now be predicted, for the different conversion levels defined in Section V.2.1, and compared to the experimental viscoelastic data. First results are shown in Fig. 11 for the three samples of Set 1. In the experimental frequency window in which the viscoelastic response can be measured, i.e. close to the terminal relaxation time of these samples, the dominant contribution to the rheological data comes from the slower segments. The predictions are based on the distributions of Fig. 10, thus assuming two conversion levels per sample. The agreement between experimental and predicted curves is quite good, i.e. the slight deviation observed at low frequencies for samples Br1-2 and Br1-3. This deviation appears when approximately 3 wt% of the sample still needs to relax, i.e. in the Constraint Release Rouse regime (see Section IV.2.3), and at the validity limit of tube models. Furthermore, it could also be due to the fact that the segments with seniority greater than 3 are disregarded.

As shown in Tables 5 and 6, the influence of the conversion level of the acid groups, $p_A$, on the sample composition is very important, especially on the proportion of segments having a large seniority. Since the viscoelastic response of the samples is expected to be very sensitive to the presence of these inner segments, one could expect a large influence of $p_A$ on their storage and loss moduli. This is indeed observed, as illustrated in Fig. 12 for the representative sample Br1-1, considered at the different conversion levels $p_A = 0.9864$, $p_A = 0.989$ and $p_A = 0.9918$. While with the last case, the sample contains 11 wt% of...
segments of seniority 2, and of mass 8.3 kg mol\(^{-1}\), which leads to a too slow relaxation of the sample, the proportion of segments of seniority 2 is only of 4.7 wt% if we consider \(p_A = 0.9864\), and their average mass \(M_{n,\text{Strand}}\) is 6.9 kg mol\(^{-1}\), which leads to a too fast relaxation compared to the experimental data. It must however be noted that as with \(p_A = 0.989\), the shape of the viscoelastic curves are similar to the shape of those for the experimental data. This is due to the fact that both curves are dominated by the Constraint Release Rouse relaxation of the linear chains and of the dangling branches, the effective average molecular weight between two entanglements \(M_e(t)\) is around \(M_c/0.08 = 25\) kg mol\(^{-1}\), which is large compared to the average molecular weight of a strand \((M_{n,\text{Strand}} = 6.91\) kg mol\(^{-1}\)).

This also explains why the agreement between experimental and predicted data for \(p_A = 0.989\) is quite good, despite the discrepancy observed in Fig. 9b, by comparing theoretical and experimental MWD. In this case, the missing high molecular weight chains in the theoretical MWD are compensated by a higher molecular weight at the peak of the distribution.

V.3 Branched PA6 samples-Set 2

V.3.1 Composition. In contrast to the first set of samples, the samples of Set 2 are all based on the same synthesis recipe but correspond to different conversion levels. In this case, the branching monomer is a triamine \((B_2)\), see Table 3. As for Set 1, there are more acid groups than amino groups in the sample (‘A’ > ‘B’). Since these samples contain both diamines \((B_2)\) and diacid \((A_2)\) as chain extenders, the linear chains and the branches of a molecule can contain a large number of successive \(A_1B_1\) strands linked by successive \(A_2\) and \(B_2\). This is illustrated in Fig. 13, for sample Br2-2 \((p_A = 0.9947)\): while, for example, a large fraction of the linear chains contain only one \(A_1B_1\) strand, some of these linear chains can contain up to 6 strands or more, linked together via \(A_2\) and \(B_2\) monomers. A similar observation is also done for the branched molecules.

This possibility of extending the chains leads to a large number of possible combinations found in the statistical ensemble of chains, which must be considered in order to correctly describe the sample and predict its rheological behavior. However, as already mentioned in Section IV.1.5, this large ensemble of molecules can be simplified by defining the chains one level up, working with “large strands”, i.e. with the molecular segments comprised between one chain end/B_3 and another chain end/B_3 (thus including the A_2 and B_2 monomers within these large strands). Indeed, due to the large number of chain extenders, the overall distribution of these large strands which contain 1, 2, or more \(A_1B_1\) strands is found to be again a Flory distribution. This is illustrated in Fig. 14 for the linear chains of sample Br2-2: summing up the MWD of the linear chains with 1, 2 or more strands leads to a Flory distribution with an average molecular weight \(M_n\) of 9.85 kg mol\(^{-1}\).

Following the same idea behind eqn (15) and (16), the average molecular weight of the large strand, \(M_{n,\text{Large Strand}}\), can then be determined by considering that the \(A_2\) and \(B_2\) monomers are now part of the large strands. Therefore:

\[
\#_{\text{Large strands}} = A_1 + A_1 + A_2 - B_2
\]

\[
M_{n,\text{Large Strand}} = \frac{A_1M_{w,A_1} + A_2M_{w,A_2} + B_2M_{w,B_2} + AB M_{w,AB}}{\#_{\text{Large Strands}}}
\]

The results obtained from these equations have been compared to the results obtained with the statistical algorithm, based on the assembling of the \(A_1B_1\) strands, and very similar values have been found. As an example, in the specific
case of sample Br2-2, eqn (23) leads to $M_{n,large \ strand} = 9.8501 \text{ kg mol}^{-1}$, very close to the value of 9.8504 kg mol$^{-1}$, found from simulation (and illustrated in Fig. 14).

Since the number of large strands per chain can directly be determined from its number of branching points (and is equal to 2Br + 1), the whole MWD of the sample as well as the classification of these large strands into different seniorities can be determined, based on the output matrices (see Section IV.1.5). Representative results are shown in Fig. 15 and in Tables 7 and 8. It must be noted that in the case of Set 2, the conversion level has been determined experimentally, based on an end-group analysis and therefore cannot be varied. From Fig. 15, it is seen that the agreement between experimental and predicted MWD is rather good. However, for increasing conversion levels, deviations at the high molecular weight side become more important. This is most probably due to a non-homogeneous solid-state post-condensation process, as compared to the linear samples and the samples of Set 1. This discrepancy is also observed in the comparison of the average molecular weight values from the experimental and predicted MWD of the whole sample, see Table 8: at high conversion level, the experimental $M_w$ becomes significantly larger than the predicted one.

From Table 7, it is seen that, as already observed in ref. 29 as well as with the first set of samples, complex molecules are mainly created at high conversion levels. We can also observe that at same conversion level, samples of Set 2 contain a smaller amount of segments deeper than 2, compared to the samples of Set 1. This difference can be explained by looking at the distribution of strands along the different segments: while the linear chains and dangling branches of samples from Set 1 contain, in large part, only one strand, the deeper segments are always composed of two strands. On the other hand, the deep generations in samples of Set 2 have, on average, the same length as the dangling branches or the linear chains, which will therefore decrease their relative proportion.

V.3.2 Viscoelastic properties. Viscoelastic data are presented in Fig. 16, and compared to their predicted behavior. As expected, the viscosity of these samples strongly increases with the conversion level, i.e. with the creation of branching architectures. Predictions have been made, based on the statistical compositions shown in Tables 7 and 8, considering a single conversion level. As observed for the MWD data, the discrepancy between predicted and experimental results increases with the conversion level since the high molecular weight tail observed in Fig. 15 is not taken into account in the predictions.

<table>
<thead>
<tr>
<th>Table 7</th>
<th>Weight proportion of different classes of segments, as a function of their conversion level, for the samples of Set 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear chains</td>
<td>Star chains</td>
</tr>
<tr>
<td>Br2-1 ($p = 0.992$)</td>
<td>46.4</td>
</tr>
<tr>
<td>Br2-2 ($p = 0.9947$)</td>
<td>36.4</td>
</tr>
<tr>
<td>Br2-3 ($p = 0.9952$)</td>
<td>34.2</td>
</tr>
<tr>
<td>Br2-4 ($p = 0.996$)</td>
<td>30.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 8</th>
<th>Predicted average molecular weight and polydispersity for samples of Set 2, as a function of their conversion level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predicted $M_n/M_w$</td>
<td>Exp. $M_n/M_w$ from SEC</td>
</tr>
<tr>
<td>Br2-1 ($p = 0.992$)</td>
<td>13.0/30.2</td>
</tr>
<tr>
<td>Br2-2 ($p = 0.9947$)</td>
<td>18.8/46.8</td>
</tr>
<tr>
<td>Br2-3 ($p = 0.9952$)</td>
<td>20.4/51.9</td>
</tr>
<tr>
<td>Br2-4 ($p = 0.996$)</td>
<td>23.9/62.9</td>
</tr>
</tbody>
</table>

Fig. 15 Samples from Set 2: predicted MWD in number ( ) and in weight ( ) versus experimental MWD in weight ( ). The predicted MWD in number are divided into the contributions of the chains classified according to their total number of strands ( ).

Fig. 16 Samples from Set 2: comparison between experimental (symbols) and predicted storage and loss moduli and complex viscosity. The predicted curves are obtained based on the statistical composition of these samples (see Tables 7 and 8) and on their measured conversion level.
VI Conclusion

The structure and rheology of branched polyamide 6 polymers are predicted, on the basis of two different reaction recipes.

To this end, a Monte Carlo approach has been first developed in order to build the different molecular architectures present in the sample, based on the initial reactant monomers and the conversion level. It consists of a two-step procedure, where initial subchains, which represent building blocks for the final molecules, are first built, before being randomly assembled. The main advantage of this approach is that it is much faster than usual Monte Carlo algorithms, without losing any information.

From this ensemble of molecules, the sample composition has been analyzed in terms of the architecture, molecular weight and seniority of the molecular segments. The same conclusion can be drawn from the two different recipes: all samples contain a large amount of linear chains, complex architectures appear only at high conversion levels, and samples after a long time of solid-state post-condensation (in order to obtain a larger conversion level) start deviating from the composition predicted based on the statistical approach. It has been shown that by combining two conversion levels, a better agreement can be obtained.

In order to predict their corresponding rheology, we proposed to use few representative segments, classified in terms of position/seniority in the molecules, rather than considering a very large ensemble of different architectures. Without losing accuracy, this approach is particularly convenient for polyamide samples since all of these molecular segments are characterized by the same (Flory) distribution. It allowed us to discuss the role of every generation in the viscoelastic behavior of the samples.

By comparing the predicted and experimental viscoelastic response, several points have indeed been discussed, such as the influence of the different architectures on the viscoelastic response or the role played by the different initial monomers. In particular, it has been shown that in most of the samples, the proportion of deep segments is too low in order to stay entangled after the relaxation of the dangling branches.

The method proposed here may be applied to any branched polymer product that is synthesized via a melt condensation type reaction and can be used as a tool to test and screen in detail the flow properties of materials without prior synthesis.

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References